

# PATENT SPECIFICATION

(11) 1 276 326

NO DRAWINGS

1 276 326

- (21) Application No. 40884/69 (22) Filed 15 Aug. 1969  
 (61) Parent of Addition to No. 1 234 641 dated 5 April 1968  
 (31) Convention Application No. 752 794 (32) Filed 15 Aug. 1968 in  
 (33) United States of America (US)  
 (45) Complete Specification published 1 June 1972  
 (51) International Classification C07C 51/10, 67/00 // B01J 11/08  
 (52) Index at acceptance

C2C 3A10A4A 3A10A4B 3A10A4E 3A10A5H  
 B1E 20Y 21X 21Y 23X 25Y 270 275 277 278 300 308 342  
 34Y 374 37Y 380 381 38Y 411 41Y 462 463 470  
 47Y 491 492 493 49Y 519 521 522 530 531 533 534  
 537 562 660



## (54) PRODUCTION OF MONOCARBOXYLIC ACIDS

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800, North Lindbergh Boulevard, St. Louis 66, State of Missouri, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of monocarboxylic acids.

Carbonylation processes for the preparation of carboxylic acids from alcohols are well known in the art and have been directed especially to the production of acetic acid. The prior art teaches the use of a number of catalysts for the synthesis of carboxylic acids by reaction of alcohols with carbon monoxide at elevated temperatures and pressures in both gas phase, fixed bed reactions and liquid phase reactions. Catalysts such as phosphoric acid, phosphates, activated carbon, heavy metal salts such as zinc and cuprous chlorides, silicates of various metals, and boron trifluoride in various hydration states have been reported to function for the production of carboxylic acids by reaction of alcohols and substituted alcohols with carbon monoxide at elevated temperatures and pressures of the order of 400°C and 10,000 psig, respectively. However, even under such severe conditions the yields of acid were somewhat poor, and, therefore, uneconomical. Somewhat less severe reaction conditions of temperature and/or pressure have been reported in the literature employing specific catalyst compositions, e.g., 330°C—340°C and 2,250 psig using liquid phosphoric acid containing copper phosphate; 300°C—500°C and 2,000—4,000 psig using active charcoal impregnated with phosphoric acid; and 260°C—360°C and 2,800 psig—15,000 psig using metal carbonyls, such as iron, cobalt and nickel

in conjunction with their halides or free halogens in the liquid phase. Even using these specific catalyst compositions at the less severe reaction conditions, substantially poorer yields of the desired carboxylic acid product and substantially slower reaction rates are obtained than those achieved in the process of this invention.

Certain disadvantages present in the carbonylation processes described in the prior art are catalyst instability, lack of product selectivity, and low levels of catalyst reactivity. One particular disadvantage of carbonylation processes of the prior art is their dependence upon the use of catalysts comprised of metal carbonyls or certain modified metal carbonyls including dicobalt octacarbonyl, iron carbonyl and nickel carbonyl, all of which require the use of high partial pressures of carbon monoxide to remain stable under the necessarily high reaction temperatures employed. For example, dicobalt octacarbonyl requires partial pressures of carbon monoxide as high as 3,000 psig to 10,000 psig under normal carbonylation conditions of 175°C to 300°C.

Still another disadvantage of carbonylation processes disclosed in the prior art is their relatively low level of activity. This low level of activity requires higher catalyst concentrations, longer reaction times, and higher temperatures to obtain substantial reaction rates and conversions. Consequently, very large and costly processing equipment is required.

Another disadvantage of carbonylation processes disclosed heretofore is their inability to maintain high selectivity to the desired carboxylic acid at temperatures required for high conversion levels and high reaction rates. At these higher temperatures undesirable by-products comprising substantial amounts of ethers, aldehydes, higher carboxylic acids, carbon dioxide, methane and water are formed, thereby resulting in substantial yield losses

and necessitating additional product purification and recycle steps in the processing.

Another disadvantage of carbonylation processes described in the prior art is their dependence on catalyst system which require the use of substantially chemically pure carbon monoxide feedstocks to maintain high selectivity and high yield to the desired carboxylic acid product. For example, certain cobalt and nickel containing catalyst systems described heretofore when employed with carbon monoxide feed streams containing impurities such as hydrogen, result in the production of a number of undesirable by-products including methane, carbon dioxide, aldehydes, alcohols of the same carbon number as the desired carboxylic acid, and carboxylic acids of higher carbon number than desired. Consequently, substantial loss in selectivity and yield to the desired carboxylic acid occurs. Catalysts of the prior art cause the formation of troublesome gaseous by-products such as carbon dioxide and methane in the reactor system, thereby suppressing the carbon monoxide partial pressure and ultimately causing a decrease in the desired carbonylation reaction rate. Often additional processing steps are required to remove these undesirable by-products, necessitating the use of larger and costlier processing equipment.

It is, therefore, an object of the present invention to overcome the above disadvantages and thus provide an improved and more economically and commercially feasible carbonylation process for the production of organic acids and their esters in liquid phase and vapor phase processes.

According to the present invention there is provided a process for the production of a monocarboxylic acid or ester thereof which comprises reacting with carbon monoxide, in the presence of a catalyst, at 125° to 250°C, a feedstock which is an alcohol of the formula  $RCH_2OH$ , or halides of the formula  $RCH_2Hal$  where Hal is chlorine bromine or iodine, where R represents phenyl, alkylphenyl,  $\alpha$ -hydroxyalkyl, etherified  $\alpha$ -hydroxyalkyl, or  $\alpha$ -haloalkyl or an ether derivative of a said alcohol or an ester derivative of a said alcohol wherein the acid moiety contains 1 to 20 carbon atoms of a 1,2-epoxy aliphatic compound, the said catalyst comprising a rhodium or iridium compound and a promoter substance selected from halogens and halogen-containing substances provided that where the feedstock is a halide of the formula  $RCH_2Hal$ , an ether or ester derivative of a said alcohol wherein R represents phenyl, alkylphenyl, etherified  $\alpha$ -hydroxyalkyl or  $\alpha$ -haloalkyl, or a 1,2-epoxy aliphatic compound, the reaction is carried out in the presence of water or an

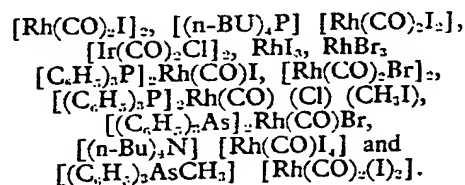
alcohol of the formula  $R-CH_2OH$  or an ether or ester derivative of a said alcohol wherein R represents  $\alpha$ -hydroxyalkyl.

More particularly according to the invention there is provided a process as just defined wherein the feedstock is a compound which contains from 2 to 30 carbon atoms.

It is to be noted that the vincinal glycols, although providing two reaction sites, yield only a monocarboxylic acid product.

The starting alcohols are reacted with carbon monoxide in the presence of an improved and more stable catalyst, thus enabling the use of lower catalyst concentration, lower temperature, lower pressure, and shorter contact time than has been generally possible heretofore and facilitating product isolation, catalyst recovery and recycle without substantial catalyst decomposition and loss. The present catalyst may be employed using a solution of the catalyst (liquid phase operation), or a solid catalyst (vapor phase operation).

The catalyst as charged to the reactor is preferably a solution containing a preformed Rh or Ir component containing a halogen promoter and other elements if desired. The catalyst preferably includes a Rh or Ir component containing a halogen, as the active component, such as

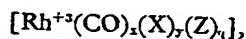


The halogen promoter portion of the present catalyst system may or may not be catalytically active in itself, but promotes the reaction in various ways, such as by facilitating cleavage of the carbon-oxygen bond in the alcohol, or, for example, by rendering the rhodium species less volatile than the unmodified rhodium carbonyl.

The active catalytic portion or first component of the preformed catalyst is prepared from rhodium or iridium species. For convenience the rhodium species will be described but it is to be understood that the corresponding iridium compounds may be used alternatively and react by methods analogous to those given for the rhodium compounds. Examples are rhodium metal, simple rhodium salts, organorhodium compounds, and coordination compounds of rhodium, specific examples of which may be taken from the following partial list of suitable rhodium or iridium precursors:

Rh metal	$[(n-C_4H_9)N][Rh(CO)_2X_2]$ where $X = Cl^-, Br^-, I^-$
$IrCl_3 \cdot 3H_2O$	$[(n-C_4H_9)_4As]_2[Rh_2(CO)_2Y_4]$ where $Y = Br^-, I^-$
$RhBr_3$	$[(n-C_4H_9)_4P][Rh(CO)I_4]$
$RhI_3$	$Rh[(C_6H_5)_3P]_2(CO)Br$
$RhCl_3 \cdot 3H_2O$	$Rh[(n-C_4H_9)_3P]_2(CO)Br$
$RhBr_3 \cdot 3H_2O$	$Rh[(n-C_4H_9)_3P]_2(CO)I$
$Rh_2(CO)_4Cl_2$	$RhBr[(C_6H_5)_3P]_3$
$Rh_2(CO)_4Br_2$	$RhI[(C_6H_5)_3P]_3$
$Rh_2(CO)_4I_2$	$RhCl[(C_6H_5)_3P]_3$
$Ir(CO)Cl(P\phi_3)_2$	$RhCl[(C_6H_5)_3P]_3H_2$
$Rh[(C_6H_5)_3P]_2(CO)I$	$[(C_6H_5)_3P]_3Rh(CO)H$
$Rh[(C_6H_5)_3P]_2(CO)Cl$	$Rh[(C_2H_4)_2Cl]_2$
$RhCl[(C_6H_5)_3P]_2(CH_3I)_2$	$K_4Rh_2Cl_2(SnCl_3)_4$
$Rh(SnCl_3)[(C_6H_5)_3P]_3$	$K_4Rh_2Br_2(SnBr_3)_4$
$RhCl(CO)[(C_6H_5)_3As]_2$	$K_4Rh_2I_2(SnI_3)_4$
$RhI(CO)[(C_6H_5)_3Sb]_2$	$Rh_2O_3, \quad IrO_2$
$[Ir(CO)_2Cl]_2$	$Rh(NO_3)_3$

The active catalytic portion or primary component of the catalyst system of this invention, as a solution, or as a supported solid catalyst, may exist as a coordination compound of Rh or Ir, carbon monoxide, and a halide (X) such as chloride, bromide and iodide,  $[Rh^{+1}(CO)_x(X)_y]$ , where  $x+y=4$ , including both neutral and ionic complexes, or a coordination compound



where  $x+y+q=5$  or  $6$ , which includes other suitable ligands (Z), if desired, such as amine, organophosphine, organoarsine, and /or organostibine ligands, other ligands, e.g., hydride; alkyl, acyl and aryl (1—20 carbon atoms); and trihalostannate or any neutral, cationic, or anionic moiety necessary to satisfy the coordination number of the central metal atom, rhodium, and thus form a coordination compound or complex of rhodium as described above. Preferred catalyst systems for the process of this invention are typically coordination complexes of rhodium, carbon monoxide and iodide, such as  $[Rh(CO)_2I_2]^-$ ,  $[Rh(CO)I_4]^-$ , or  $[Rh(CO)_2I]_2$ .

The term coordination compound or coordination complex used throughout this specification means a compound or complex formed by combination of one or more electronically rich molecules or atoms capable of independent existence with one or more electronically poor molecules or atoms, each of which may also be capable of independent existence.

The promoting portion or second component of the catalyst system consists of a halogen and may be supplied as a halogen compound such as hydrogen halide, alkyl- or aryl-halide, metal halide, ammonium, phosphonium, arsonium and stibonium halide, and may be the same or different from any halogen component already present in the precursor Rh or Ir component of the catalyst system. Halogen or halide compounds are suitable for the promoter portion of the catalyst, but those containing iodine and bromine are preferred, with hydrogen iodide constituting a more preferred member. Accordingly, suitable compounds providing the promoter portion of the catalyst system of this invention may be selected from the following list of preferred halogen and/or halogen containing compounds:

$RX_n$ (n is 1 to 3)	where	R = any alkyl-, alkylene- or aryl group	e.g., $CH_3I$ , $C_6H_5Br$ , $CH_2CH_2I$ , $ICH_2CH_2I$ , etc.
	and	X = Cl, Br, or I	
$X_2$ or $X_3^-$	where	X = Cl, Br, or I	e.g., $Br_2$ , $I_2$ , $I_3^-$ , etc.
HX	where	X = Cl, Br, or I	e.g., HBr, HI
$\begin{array}{c} RCX \\    \\ O \end{array}$	where	R = any alkyl- or aryl-group	e.g., $CH_3Cl$ , etc. $\begin{array}{c}    \\ O \end{array}$
	and	X = Cl, Br, or I	
$R_4MX$ , $R_4MX_3$ , or $R_3MX_2$	where	R = hydrogen or any alkyl- or aryl-group	e.g., $NH_4I$ , $PH_4I_3$ , $PH_3I_2$ , $PH_3Br_2$ ,
		M = N, P, As or Sb	$(C_6H_5)_3PI_2$ , and /or combinations of R, M and X
		X = Cl, Br or I	

5 The promoter portion or second component of the catalyst may alternatively be charged to the reactor separately from the active catalyst or first component, or it may be incorporated into the active component, e.g.,



10 The rhodium or iridium compound or first component of the catalyst system may be prepared prior to charging the reactor or generated *in situ*. Subsequently, after the first component is in the reactor and dissolved in a suitable solvent, the promoter or second component of the catalyst may be added as a solid or liquid  
15 compound, or in solution in a suitable solvent compatible with that already employed in the process of this invention. However, the promoter portion of the catalyst may also be incorporated in the active catalyst or first component either during the preforming or during the *in situ* generation of the metal complex.

20 The preparation of the active catalyst complex which includes both rhodium and iridium and halogen promoter components may be accomplished by a variety of methods. However, it is thought that a substantial part of the precursor rhodium or iridium component is

converted to the monovalent state during the preparative treatment. In general, in the process of this invention, it is preferable to preform the active carbonylation catalyst system which contains both rhodium or iridium and halogen promoter components. For example, to prepare the catalyst system, the first component of the catalyst system, e.g., finely divided rhodium metal (powder), a simple rhodium salt or rhodium compound as a precursor is dissolved in a suitable medium, and carbon monoxide is bubbled through the above rhodium solution, preferably while maintaining gentle heating and stirring of the rhodium solution. Then an acidic solution of the desired halogen promoter is added to form an active catalytic solution containing the necessary rhodium and halogen promoter components.

Generally, any preformed rhodium compound may be charged to the reactor directly and, if desired, is dissolved in an appropriate solvent. If desired, the rhodium coordination compounds described above may be prepared from any of the simpler types of rhodium salts. For example, to prepare the catalyst system, the first component of the catalyst system, e.g., a rhodium salt such as  $RhCl_3 \cdot 3H_2O$  is dissolved in a suitable solvent

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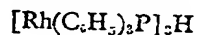
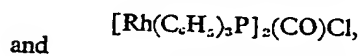
such as ethanol. Subsequently, carbon monoxide is bubbled through the solution where an intermediate, such as the dimer



5 is produced wherein the rhodium is in the monovalent state. The second or promoter component is, for example, added to the above solution, e.g., as aqueous HI, or methyl iodide or other halogen containing compound.

10 Alternatively, the rhodium precursor, e.g.,  $\text{RhCl}_2 \cdot 3\text{H}_2\text{O}$  or  $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , may be dissolved in a dilute aqueous acid solution, e.g. HCl, and acetic acid, as solvent. Then the solution of the rhodium compound is heated, for example, to  $60^\circ\text{C}$ — $80^\circ\text{C}$ , or in general at a temperature below the boiling point of the solvent, with stirring. A reducing agent such as carbon monoxide is bubbled through the said solution to obtain the rhodium component at least in part in the monovalent state. The halogen promoter is added as described herein, although the halogen containing promoter may also be added first.

25 Another embodiment of the present invention employs compounds of monovalent rhodium initially, wherein the transformation to active catalyst does not involve a change of valence. For example, monovalent rhodium salts such as



35 are dissolved in a suitable solvent and carbon monoxide is subsequently passed through a solution that is preferably warmed and stirred. Subsequent addition of an acidic solution of the halogen promoter, e.g., methyl iodide, methyl bromide, aqueous HI and HBr., results in formation of an active carbonylation catalyst solution containing the necessary rhodium and halogen components.

40 Alternate embodiments of the present invention include use of other rhodium components in various oxidation states, e.g., rhodium metal (zero valence state), rhodium salts, e.g.,  $\text{RhI}_3$  (+3 valence state), other rhodium compounds, e.g., tris - acetylacetonato rhodium (III) (+3 valence state); with 50 suitable chemical reagents to accomplish the desired transformation to the monovalent rhodium state. Such reagents include reducing agents, e.g., hydrogen, carbon monoxide, hydrazine, formic acid and phenylhydrazine; and oxidizing agents, e.g., elemental halogens ( $\text{I}_2$  or  $\text{Br}_2$ ), mineral acids, (HCl, HBr,  $\text{HNO}_3$ , HI), peroxides ( $\text{H}_2\text{O}_2$ , and cumene hydroperoxide).

This catalytic solution containing

60 the necessary rhodium and halide components is then ready for use as discussed above. Often it may be beneficial and desirable to have the concentration of the second component or promoter portion of the catalyst system, for example, iodide such as HI or  $\text{CH}_3\text{I}$ , in excess 65 of that required to form a stoichiometric compound such as described above. In the same way the two components, e.g., a rhodium compound and an iodine or bromine component are provided in a single molecule by beginning 70 with rhodium triiodide or rhodium tribromide as the catalyst precursor for the reaction of an alcohol with carbon monoxide to produce an organic acid. The present discussion is based upon the catalyst precursors as charged. The 75 ultimate nature of the catalyst as modified by reaction conditions, and the presence of promoters and reactants has not been completely elucidated. However, it has been found that the use of the components described herein 80 provides a highly superior catalyst and process for the production of carboxylic acids.

Although any ratio of promoter portion or second component of the catalyst system may be employed, ratios of promoter portion to active portion expressed as atoms of halogen 85 in the promoter portion to atoms of rhodium or iridium in the active portion of the catalytic system in the range of 1:1 to 2500:1 are generally employed. However, the preferred range is 3:1 to 300:1 halogen atoms 90 per rhodium or iridium atom.

The liquid reaction medium employed may be any solvent compatible with the catalyst system and may include pure alcohols, or mixtures of the alcohol feedstock and/or the 95 desired carboxylic acid and/or esters of these two compounds or other carboxylic acids such as acetic acid. The preferred solvent and liquid reaction medium for the process of this invention is a monocarboxylic acid having 100 2—6 carbon atoms, e.g., acetic, propionic, butyric, pentanoic and hexanoic acids, including isomeric forms. Water may also be added to the reaction mixture to exert a beneficial effect upon the reaction rate. Other liquid 105 phase reaction media may be chosen such as the organo-phosphorus ligands employed in preparation of the catalyst system. An example of such a ligand which may function as the liquid reaction medium and/or solvent is triphenylphosphite. 110

Examples of preferred feedstocks employed for the carbonylation reaction of the present invention include the group of substituted 115 alcohols such as benzyl alcohol to yield phenylacetic acid; 1,2 - ethylene glycol to yield propionic acid; 1,2 - propylene glycol to yield butyric acid, methylbenzyl alcohol to yield tolylacetic acid; and derivatives of substituted alcohols such as ethylene oxide to yield propionic acid; benzyl chloride or iodide 120 to yield phenylacetic acid; 2 - methoxyethanol

and 1,2 - dimethoxyethane to yield propionic acid; 1,2 - butyleneoxide to yield valeric acid; benzylacetate to yield phenylacetic acid and ethylenechlorohydrin to yield propionic acid and 1,2 - dibromobutane to yield *n* - valeric acid.

The carbonylation reaction may be carried out by intimately contacting an alcohol or alcohol derivative, as set forth above, which depending on the carbon number and operating conditions may either be in the vapor or liquid phase, with gaseous carbon monoxide in a liquid phase containing the catalyst system prepared from  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  or other rhodium or iridium components as precursor, in the presence of halogen containing promoter, such as hydrogen iodide, under conditions of temperature and pressure suitable as described herein to form the carbonylation product. The particular conditions selected are the same whether the feedstock is charged as a vapor or liquid. The temperature accordingly will be in the range of  $125^\circ\text{C}$  to  $250^\circ\text{C}$  with the preferred range being  $165^\circ\text{C}$  to  $225^\circ\text{C}$ . Partial pressures of carbon monoxide of the order of 5 psig to 5,000 psig may be employed; however, 75 psig to 1,000 psig carbon monoxide partial pressure is generally preferred. Higher pressures may be used if desired under appropriate conditions.

Alternatively, carboxylic acids may be produced if desired via reaction of the substituted alcohols or alcohol derivatives, together with carbon monoxide in the vapor phase over the rhodium or iridium containing catalyst systems described above, dispersed upon inert supports. Such a catalyst system may be operated as a conventional fixed bed catalytic reactor. For example, ethylene oxide, hydrogen iodide, and carbon monoxide may be passed over a catalyst system consisting, for example, of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  dispersed on an inert support material such as Alundum (Registered Trade Mark), activated carbon, clays, alumina, silica-alumina, and ceramics, in a fixed bed reactor maintained at elevated temperature and pressure, as described above, to produce propionic acid in high yield. However, use of a liquid reaction medium is preferred in the process of this invention using dissolved or dispersed active catalytic and promoter components.

A typical carbonylation reaction selective to monocarboxylic acid requires at least one mole of carbon monoxide per mole of substituted alcohol or alcohol derivative. Excess of carbon monoxide over the aforesaid stoichiometric amount, however, may be present. Carbon monoxide streams containing inert impurities such as hydrogen, carbon dioxide, methane, nitrogen, noble gases, water and paraffinic hydrocarbons having from 1 to 4 carbon atoms, may be employed, if desired, for example, from an available plant gas stream, with no ill effect; however, in such cases total reactor pressure will have to be increased to

maintain a desired carbon monoxide partial pressure. The concentration of carbon monoxide in the feed gas mixture may be from 1 vol. % to 99.9 vol. %, a preferred range being from 10 vol. % to 99.9 vol. %.

The reaction rate is dependent upon catalyst concentration and temperature. Concentrations of the rhodium or iridium compound or the first component of the catalyst system in the liquid phase, between  $10^{-6}$  moles/liter and  $10^{-1}$  moles/liter, are normally employed, with the preferred range being  $10^{-4}$  moles/liter to  $10^{-2}$  moles/liter. Higher concentrations even to the extent of 1 mole/liter may, however, be used if desired. Higher temperatures also favor higher reaction rates. The concentration of the second component or promoter portion of the catalyst system may vary widely over the broad concentration range of  $10^{-6}$  moles/liter to 18 moles/liter, based on halogen atom. In the process of this invention, however, the preferred concentration range of promoter is  $10^{-1}$  moles/liter to 2 moles/liter of catalyst solution.

The active rhodium or iridium catalytic component is preferably supplied as a catalyst solution. The solution can also include liquid reactants, products and mixtures thereof which function as solvents or reaction media.

When an ester or half-ester of the substituted alcohol is present in the feedstock, such as 2 - methoxyethanol or 1,2 - dimethoxyethane, it is normally charged with equimolar amounts of water, although more or less water may be used. The use of the ester is on the basis that a molar quantity of water is present equivalent to the number of equivalents of ester present. It has been found that water generally exerts a beneficial effect on the rate of reaction. However, adding water, with the feed in excess of the equimolar quantity, e.g., an excess of 50% to 300% of such equimolar quantity, already present with ester, as discussed above, promotes the production of acid.

The rhodium and iridium catalysts of the present invention are characterized by a high degree of specificity for the carbonylation reaction, e.g., the reaction of alcohol groups with carbon monoxide to obtain monocarboxylic acids or vicinal glycols to yield monocarboxylic acids. Such control over the various competing reactions to obtain the monocarboxylic acid in high yield, with the repression of dicarboxylic acid formation, is surprising since other metal catalysts do not show such specificity. The iron group metals such as iron, cobalt and nickel differ from the present rhodium and iridium catalysts in that the iron group metals simultaneously catalyze hydrogenation reactions to a very high degree. Furthermore, the iron group catalysts, particularly cobalt and nickel, require a far higher carbon monoxide partial pressure to remain stable. When moderate pressures, e.g., less than about 2,000 psig carbon monoxide partial pressure

are employed, at a temperature of 175°C, the cobalt catalyst is found to plate out or decompose to the free metal which plates on the walls of the reactor and is thus lost as a catalyst. In addition, the iron group catalysts when employed with vicinal glycol feedstocks, e.g., 1,2 - ethylene glycol, result in formation of large proportions of dicarboxylic acids such as succinic acid.

Another distinction of the rhodium and iridium catalysts over the cobalt catalysts is the elimination of undesirable gaseous by-products, including carbon dioxide and methane which are obtained as a result of the water-gas shift reaction which is strongly catalyzed by cobalt.

The discussion herein relating to production of carboxylic products includes production of derivatives, such as esters by reaction of the desired carboxylic acid with an alcohol moiety which may be the same or different from the feedstock, and is carried out *in situ* in the reactor by control of alcohol conversion or accomplished separately by subsequent reaction in a separate vessel.

For a better understanding of the process of the present invention specific embodiments of the process are presented below. These examples and illustrations are not to be construed in any way as limiting the scope of the invention.

#### EXAMPLE 1

A batch reactor is charged with the following ingredients: 0.396 grams of a rhodium compound having the formula  $\text{RhCl}_2 \cdot 3\text{H}_2\text{O}$ , 51 grams of a promoter consisting of aqueous 57 wt. % hydriodic acid, 196.9 grams of acetic acid as a solvent, and 100 grams of benzyl alcohol as feedstock.

The reactor is pressurized with carbon monoxide to a total pressure of 1,000 psig,

corresponding to a carbon monoxide partial pressure of about 800 psig, at the reaction temperature of 175°C. The reaction is carried out at constant pressure. The reaction products are subsequently analyzed by gas chromatographic techniques.

The selectivity to the formation of the desired carboxylic acid product, phenylacetic acid, is greater than 85 mol %. No substantial amounts of by-products such as aldehydes, higher boiling carboxylic acids, methane, or carbon dioxide are formed.

When this experiment is conducted with the equivalent molar quantity of cobalt chloride instead of rhodium chloride as the catalyst, the selectivity and yield of the desired acid product are decreased significantly. It has been found that cobalt catalysts differ radically from rhodium catalysts in that the cobalt catalysts also cause hydrogenation reactions such as hydrogenation of the desired carboxylic acid product to aldehydes and alcohols of the same number of carbon atoms. Consequently, the use of cobalt catalysts results in the substantial production of various undesirable by-products including higher carbon number alcohols, carboxylic acids, and derivatives.

Still another distinction of the rhodium catalysts compared to the cobalt and nickel catalysts is the fact that significantly lower carbon monoxide partial pressure can be used without encountering catalyst decomposition.

#### EXAMPLES 2—12

The procedure of Example 1 is also followed in detailed Examples 2—12, in order to illustrate the variation of parameters. Data of these runs are shown in the accompanying table, including variation of catalyst components, feedstock, and reaction conditions along with results for product selectivity. The symbol  $\phi$  means phenyl.

TABLE

Run Conditions: [Rh or Ir]  $\times 10^{-3}$  M; [Br or I] 0.6 M; 50 ml solvent; Time: 17 hours

Ex.	Feedstock	Catalyst Precursor		Solvent	Temp. °C.	Reactor Press. psig	Major Product Selectivity (mol %)
		Rh	Promoter				
2	$\text{HO}(\text{CH}_2)_2\text{OH}$	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	HI	$\text{CH}_3\text{COOH}$	175	700	$\text{CH}_3\text{CH}_2\text{COOH}$ (95)*
3	$\text{HOCH}_2\text{CH}(\text{CH}_3)\text{OH}$	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	HI	$\text{CH}_3\text{COOH}$	200	1,000	$\left[ \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \\ \text{CH}_3\text{CHCOOH} \\   \\ \text{CH}_3 \end{array} \right] - (95)^*$
4	$\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}$	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	HI	$\text{CH}_3\text{COOH}$	215	1,100	$\text{CH}_3\text{CH}_2\text{COOH}$ (47)*
5	$\text{HOCH}_2\text{CH}(\text{CH}_2)_3\text{CH}_3$ $\text{OH}$	$\text{Rh}(\text{P}(\phi_3)_3)_2\text{COCl}$	$\text{CH}_3\text{I}$	$\text{CH}_3\text{CH}_2\text{COOH}$	200	1,000	$\left[ \begin{array}{c} \text{CH}_3(\text{CH}_2)_4\text{COOH} \\ \text{CH}_3(\text{CH}_2)_3\text{CHCOOH} \\   \\ \text{CH}_3 \end{array} \right] - (65)^*$
6	$\phi\text{CH}_2\text{OH}$	$[\text{Ir}(\text{CO})_2\text{Cl}]_2$	HI	$\text{CH}_3\text{COOH}$	175	700	$\phi\text{CH}_2\text{COOH}$ (83)*
7	$\phi\text{CH}_2\text{OH}$	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	HI	$\text{CH}_3\text{COOH}$	140	500	$\phi\text{CH}_2\text{COOH}$ (90)*
8	$\phi\text{CH}_2\text{I}$	$[\text{Rh}(\text{CO})_2\text{Br}]_2$	HI	$\text{CH}_3\text{CH}_2\text{COOH}$	175	300	$\phi\text{CH}_2\text{COOH}$ (83)*
9	$\text{CH}_2=\text{CH}-\text{CH}_2$ $\text{O}$	$\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	$\text{CaI}_2 \cdot 3\text{H}_2\text{O}$	$\text{CH}_3\text{COOH}$	200	1,000	$\left[ \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \\ \text{CH}_3\text{CHCOOH} \\   \\ \text{CH}_3 \end{array} \right] - (88)^*$
10	$\text{ClCH}_2\text{CH}_2\text{OH}$	$\text{Rh}(\text{P}(\phi_3)_3)_3\text{Cl}$	HI	$\text{CH}_3\text{CH}_2\text{COOH}$	200	800	$\text{CH}_3\text{CH}_2\text{COOH}$ (93)*
11	$\text{CH}_3\phi\text{CH}_2\text{OH}$	$\text{Rh}_2\text{O}_3$	HBr	$\text{CH}_3\text{COOH}$	165	600	$\text{CH}_3\phi\text{CH}_2\text{COOH}$ (82)*

\*No dicarboxylic acids formed as determined by chromatographic analysis.



## EXAMPLE 12

A solid supported catalyst containing an iridium component and a halogen promoter dispersed upon an inert support is prepared in the following manner: An amount of 0.6 g. of an iridium compound, having the formula  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ , is dissolved in 2 - methoxy ethanol. The solution is warmed to 60°C, and carbon monoxide is bubbled through the solution until a pale yellow color is obtained indicating the presence of the monovalent complex. Then the solution is cooled and 20 ml of 57 wt. % hydriodic acid is added to the solution of the iridium compound. Subsequently, the resulting solution is added to 20 ml of an activated carbon (Pittsburgh Activated Carbon Co.). The excess solvent is evaporated using a rotary evaporator under vacuum. The resulting catalyst is vacuum dried at 60°C for about 16 hours. The catalyst is then preheated in nitrogen at 200°C for one hour.

Ten (10) ml of the above supported catalyst is charged into an 18-inch Pyrex (Registered Trade Mark) glass vertical reactor 30 mm in diameter. The resulting catalyst bed, 2 cm in depth, is covered with 100 ml of inert packing as a preheater. Gaseous ethylene oxide is supplied to the reactor and is subsequently converted to propionic acid at high selectivity. The process is conducted at a feed rate (moles per hour) of ethylene oxide, 0.14;  $\text{HI}$ , 0.02; water, 0.28; and  $\text{CO}$ , 0.54. The pressure at which the gaseous reactants contact the supported catalyst is 500 psig, corresponding to a carbon monoxide partial pressure of about 125 psig at a reaction temperature of 175°C.

The gaseous reactor effluent contains the desired carboxylic acid product, propionic acid, and unreacted ethylene oxide, water, carbon monoxide and promoter. The selectivity of ethylene oxide conversion to propionic acid is virtually quantitative.

When this example is repeated except that hydrogen gas is used as a 50 vol. % diluent in the feedstream, similar results are obtained.

## WHAT WE CLAIM IS:—

1. A process for the production of a monocarboxylic acid or ester thereof which comprises reacting with carbon monoxide, in the presence of a catalyst, at 125 to 250°C, a feedstock which is an alcohol of the formula  $\text{RCH}_2\text{OH}$ , or halide of the formula  $\text{RCH}_2\text{Hal}$  where Hal is chlorine, bromine or iodine, where R represents phenyl, alkylphenyl,  $\alpha$  - hydroxy alkyl, etherified  $\alpha$  - hydroxyalkyl, or  $\alpha$  - haloalkyl or an ether derivative of a said alcohol or an ester derivative of a said alcohol wherein the acid moiety contains 1 to 20 carbon atoms, or a 1,2 - epoxy aliphatic compound, the said catalyst comprising a rhodium or iridium compound and a promoter substance selected from halogens and halogen-

containing substances provided that where the feedstock is a halide of the formula  $\text{RCH}_2\text{Hal}$ , an ether or ester derivative of a said alcohol wherein R represents phenyl, alkylphenyl, etherified  $\alpha$  - hydroxyalkyl or  $\alpha$  - haloalkyl, or a 1,2 - epoxy aliphatic compound, the reaction is carried out in the presence of water or an alcohol of the formula  $\text{RCH}_2\text{OH}$  or an ether or ester derivative of a said alcohol wherein R represents  $\alpha$ -hydroxyalkyl.

2. A process according to claim 1 wherein the feedstock is a compound as defined in claim 1 which contains from 2 to 30 carbon atoms.

3. A process according to claim 1 wherein the feedstock comprises benzyl alcohol.

4. A process according to claim 1 wherein the feedstock comprises 1,2-ethylene glycol.

5. A process according to claim 1 wherein the feedstock comprises 1,2-propylene glycol.

6. A process according to claim 1 wherein the feedstock comprises methyl benzyl alcohol.

7. A process according to claim 1 wherein the feedstock comprises ethylene oxide.

8. A process according to claim 1 wherein the feedstock comprises benzyl iodide.

9. A process according to claim 1 wherein the feedstock comprises 2 - methoxy ethanol.

10. A process according to claim 1 wherein the feedstock comprises 1,2 - dimethoxy ethane.

11. A process according to claim 1 wherein the feedstock comprises 1,2 - butylene oxide.

12. A process according to claim 1 wherein the feedstock comprises benzyl acetate.

13. A process according to claim 1 wherein the feedstock comprises ethylene chlorhydrin.

14. A process according to claim 1 wherein the feedstock comprises 1,2 - dibromo butane.

15. A process according to claim 1 wherein the feedstock comprises benzyl chloride.

16. A process according to any of claims 1—15 wherein the catalyst is in solution and the reaction is effected in the liquid phase.

17. A process according to claim 16 wherein the liquid phase includes water.

18. A process according to any of claims 1—17 wherein the reaction is effected at a partial pressure of carbon monoxide of 5 psig to 5000 psig.

19. A process according to claim 18 wherein the pressure is 75 psig to 1000 psig.

20. A process according to any of claims 1—19 wherein the catalyst comprises a rhodium halide.

21. A process according to any of claims 1—19 wherein the catalyst comprises a rhodium carbonyl halide.

22. A process according to any of claims 1—19 wherein the catalyst comprises rhodium trichloride or rhodium tri-iodide.

23. A process according to any of claims 1—19 wherein the catalyst comprises a

monoxide and a halogen ligand selected from chlorine, bromine or iodine.

24. A process according to any of claims 1—19 wherein the catalyst comprises an iridium carbonyl halide.

25. A process according to any of claims 1—19 wherein the catalyst comprises iridium trichloride or iridium tri-iodide.

26. A process according to any of claims 1—19 wherein the catalyst comprises an iridium compound which comprises carbon monoxide and a halogen ligand selected from chlorine, bromine and iodine.

27. A process according to any of the preceding claims wherein the promoter substance is iodine or an iodine compound.

28. A process according to claim 27 wherein the promoter substance is hydrogen iodide.

29. A process according to any of the preceding claims wherein, in the catalyst, the ratio of atoms of halogen in the promoter substance to atoms of rhodium or iridium is in the range of 1:1 to 2500:1.

30. A process according to claim 29 wherein the said range is 3:1 to 300:1.

31. A process according to any of the preceding claims, effected in the liquid phase, wherein the catalyst is in solution and is at a concentration, in terms of rhodium or iridium between  $10^{-6}$  and  $10^{-1}$  moles/litre.

32. A process according to claim 31 wherein the said range is  $10^{-1}$  to  $10^{-2}$  moles/litre.

33. A process according to any of claims 1—30, effected in the liquid phase, wherein the concentration of promoter substance is  $10^{-6}$  to 18 moles/litre based on the halogen atom.

34. A process according to claim 33 wherein the said range is  $10^{-1}$  to 2 moles/litre.

35. A process according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing specific Examples 1—12.

36. A monocarboxylic acid prepared by a process as defined in any of the foregoing claims 1—35.

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8, Staple Inn, London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.